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AND
TWO TATB-BASED EXPLOSIVES

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A THERMOGRAVIMETRIC STUDY OF TATB
AND
TWO TATB-BASED EXPLOSIVES

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INTRODUCTION

Basic physical properties of TATB (1,3,5-triamino, 2,4,6-trinitrobenzene) and TATB-based PBX's (plastic-bonded explosives) are needed, particularly to provide valid estimates of their long term thermal stability. We have studied the thermal behavior in vacuum by measuring the vapor pressures of TATB and two TATB-based PBX's. The equilibrium sublimation pressures and heats of sublimation of TATB and PBX's were determined in the temperature range of 150-200°C.

EXPERIMENTAL

The compositions of the materials selected for study are given in Table 1.

Table 1. Materials Studied

DESIGNATION	BINDER	VOL% BINDER	WT% BINDER
TATB	---	---	---
RX-03-BB	KEL-F 800	7.2	7.5
RX-03-DI	PHENOXY-PKHJ	6.0	3.7

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A thermogravimetric analysis-residual gas analysis (TGA-RGA) system consisting of a high-sensitivity electrobalance (CAHN R-100) and a quadrupole residual gas analyzer (UTI-100C) was used to perform the experiments. The experimental arrangement is shown schematically in Figure 1.

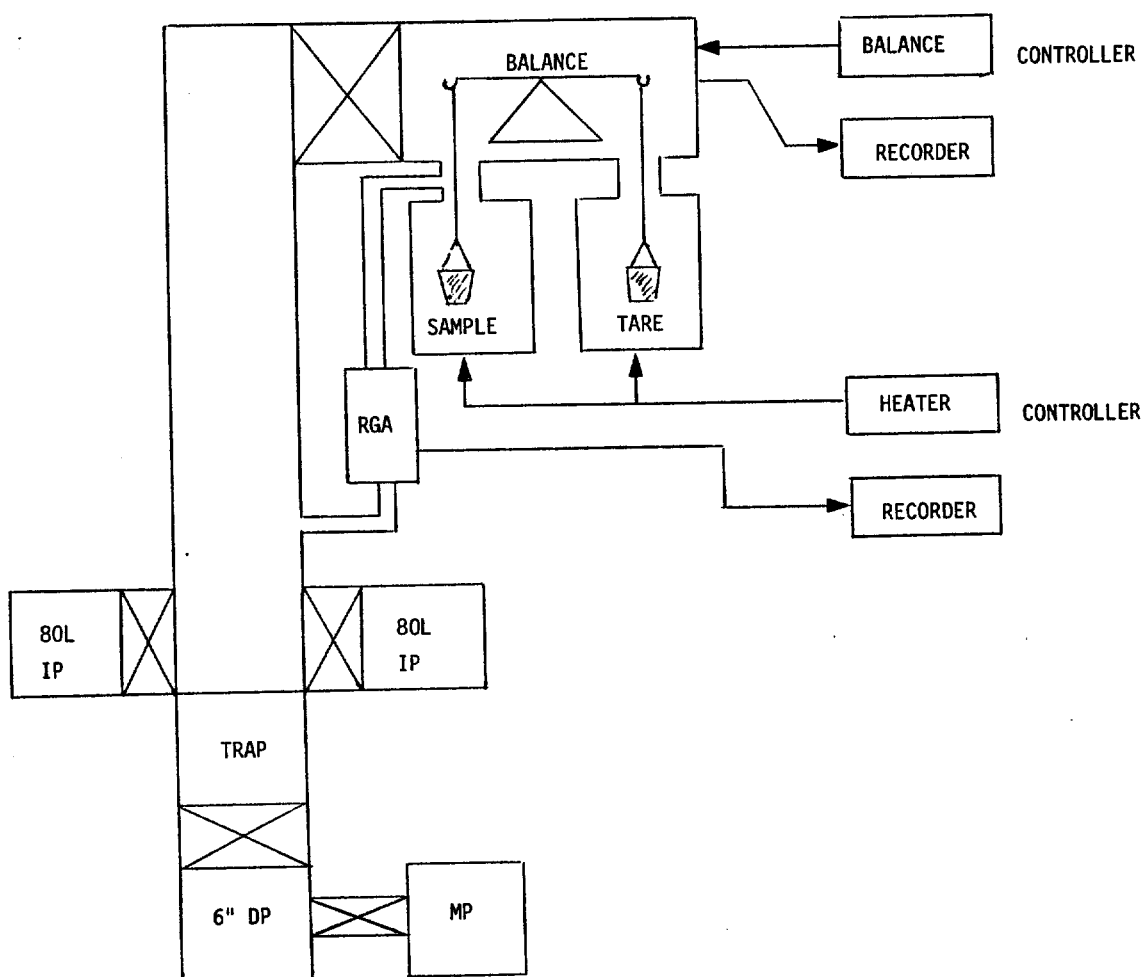


Figure 1. TGA-RGA System

Samples were enclosed in a Knudsen cell (orifice $r = 0.50$ mm) as shown in Figure 2. The cell used had the following dimensions: ID = 9 mm, OD = 10 mm, height = 10 mm, and orifice diameter = 1 mm. The temperature was attained by use of a cylindrically wound heater inside the vacuum vessel that was provided with stainless steel shields inside and outside the heater support ring.

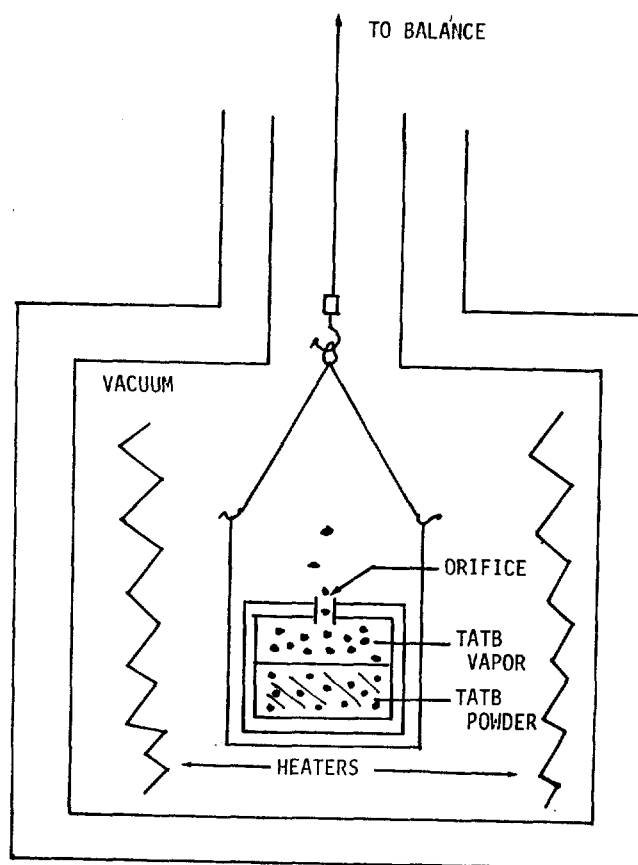


Figure 2. Sample Cell

A thermocouple was welded to the inner heater shield and another was located closely below, but not in contact with, the sample cell. Sample and heater temperatures were automatically controlled.

The Knudsen cell was half-filled with a sample powder and placed in the TGA-RGA system. The system was then pumped down to less than 1×10^{-6} torr while the temperature was kept in the range of 25-45°C. Heating was then initiated and isothermal conditions were attained in about 80 minutes. The effusion weight loss was recorded dynamically with the microbalance at 150, 175 and 200°C. The evolution of volatile species was monitored with the residual gas analyzer.

RESULTS

The vapor pressure of an explosive was determined from weight loss of the sample. A typical weight loss curve for RX03-BB is shown in Figure 3.

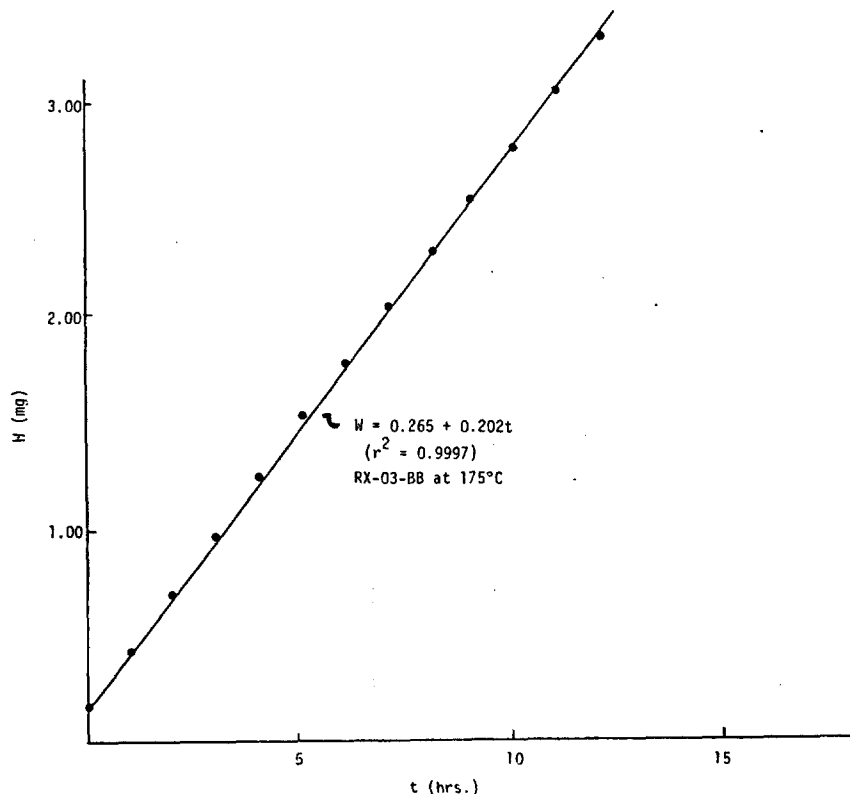


Figure 3. Weight loss of RX03-BB at 175°C

The Knudsen equation was used to determine vapor pressures from the effusion weight loss data. The equation used is

$$P = W \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where, P = vapor pressure (in torr)
 W = rate of effusion (in g/cm² sec)
 T = temperature (K)
 R = gas constant (cal/mole K)
 M = molecular weight of effusing species in (g/mole)

The effusing species was assumed to be TATB in all cases. This was confirmed by analysis of the sublimed material using ESCA, x-ray diffraction, mass spectroscopy, and IR spectroscopy techniques.

The calculated vapor pressures for the three explosives studied are presented in Table 2. The values represent single measurements. The range given for each value is an estimate of the precision based on instrumental characteristics.

Table 2. Vapor Pressure in Torr at T (°C)

	150	175	200
TATB	1.0(±0.2)×10 ⁻⁶	2.4(±0.2)×10 ⁻⁵	2.1(±0.1)×10 ⁻⁴
RX03-DI	2.0(±0.2)×10 ⁻⁶	1.8(±0.1)×10 ⁻⁵	2.0(±0.1)×10 ⁻⁴
RX03-BB	1.1(±0.2)×10 ⁻⁶	2.2(±0.1)×10 ⁻⁵	2.0(±0.1)×10 ⁻⁴

The same data is shown graphically in Figure 4 for comparison of pure TATB to its two PBX's. A line of best fit to our pure TATB data is shown as well as the data of Rosen & Dickinson⁽¹⁾ for TATB.

Our values for the heat of sublimation of the three explosives and the value reported by Rosen & Dickinson for pure TATB are shown in Table 3.

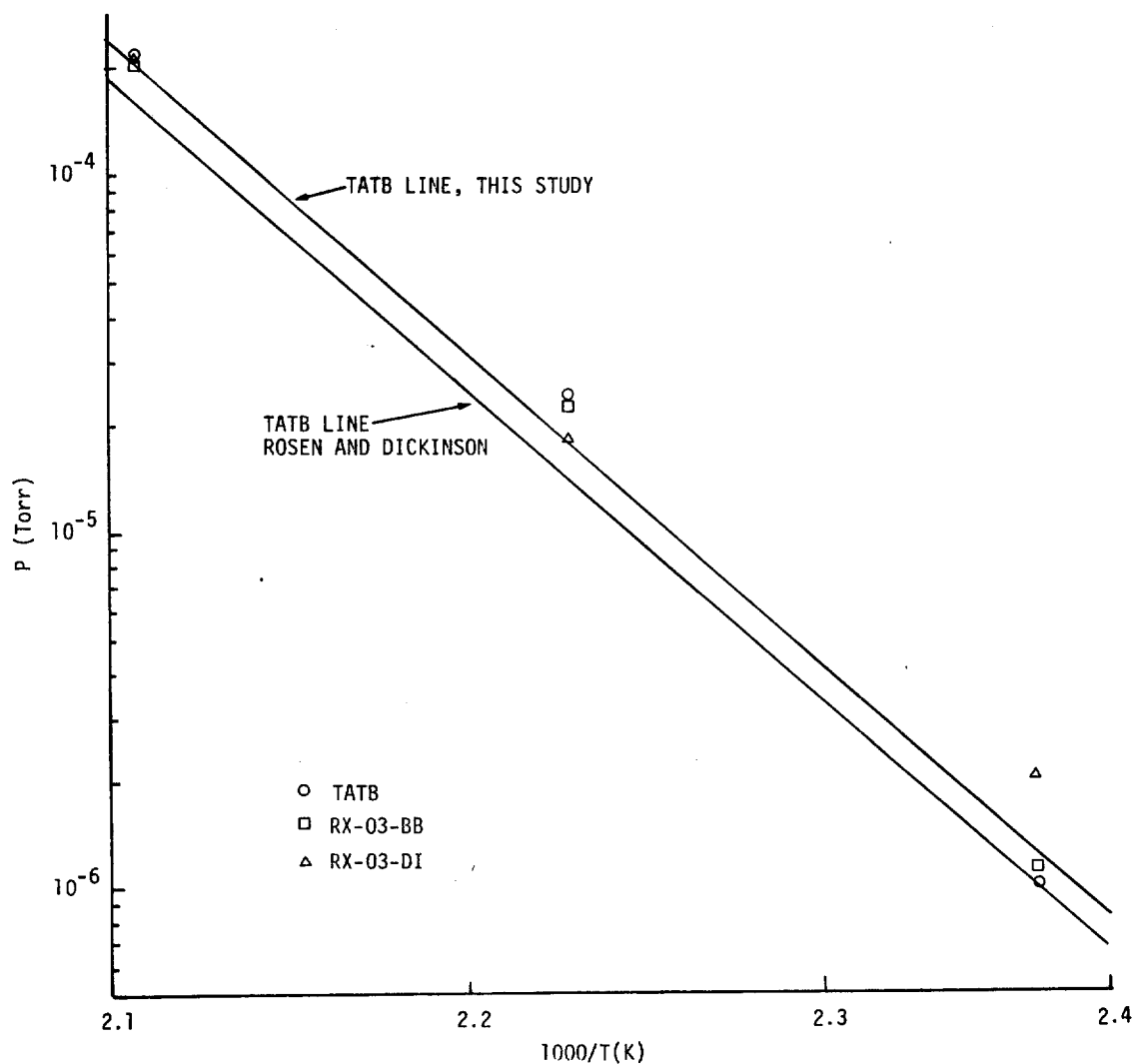


Figure 4. Vapor Pressures

⁽¹⁾J. M. Rosen & C. Dickinson, J. Chem. Eng. Data 14, 20 (1969).

Table 3. Heat of sublimation

MATERIAL	H _s (Kcal/Mole)	SOURCE
TATB	43.1	THIS WORK
TATB	40.2	ROSEN & DICKINSON
RX-3-BB	41.1	THIS WORK
RX-03-D1	36.9	THIS WORK

Some residual gas analysis spectra of gases from TATB at 20, 150 and 200°C are displayed in Figure 5. The principal ion fragment is at mass 18 (i.e., water). The normalized intensity (I/I_{\max}) of mass 18 is graphed as a function of time in Figure 6.

The desorption of water from the heater and shields as they begin to heat up is seen as the initial large peak. A similar surface desorption is seen as a smaller peak when the sample begins to heat. Once isothermal sample conditions are reached, the water signal presumably represents the bulk behavior of the sample.

The isothermal evolution of water from TATB is shown in Figure 7, where normalized mass 18 intensity is plotted versus $\sqrt{t-t_{\text{iso}}}$. According to Fick's law a diffusion controlled process is described by

$$q \propto \sqrt{D/\pi t} \quad (2)$$

where, q = outgassing rate

D = diffusion coefficient

t = time

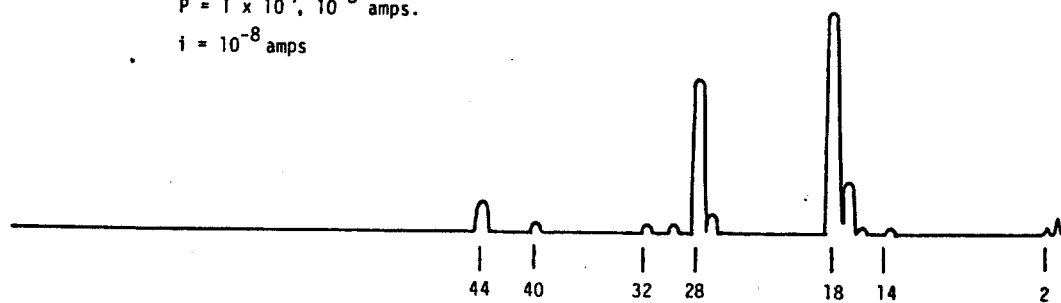
TATB AFTER 10 HOURS

AT 200°C.

$P = 1 \times 10^{-7}$, 10^{-8} amps.

$i = 10^{-8}$ amps

-8

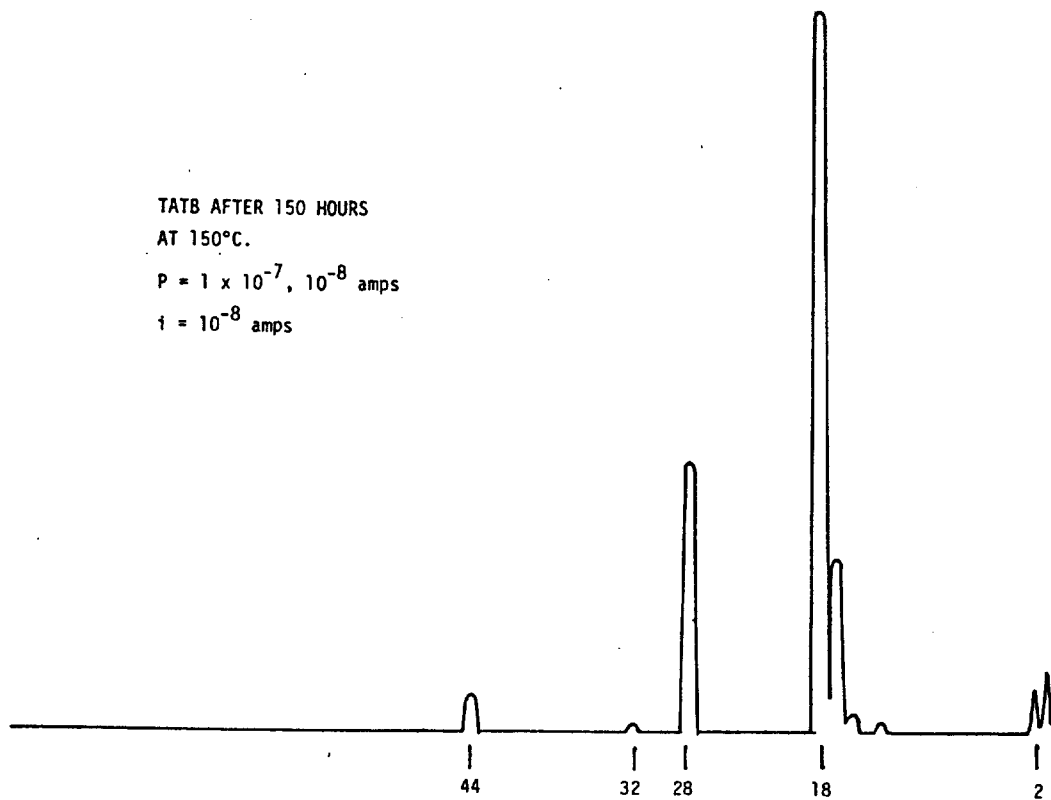


TATB AFTER 150 HOURS

AT 150°C.

$P = 1 \times 10^{-7}$, 10^{-8} amps

$i = 10^{-8}$ amps



TATB BEFORE HEATING.

at 20°X

$P = 1 \times 10^{-6}$ Torr

$i = 10^{-7}$ amps

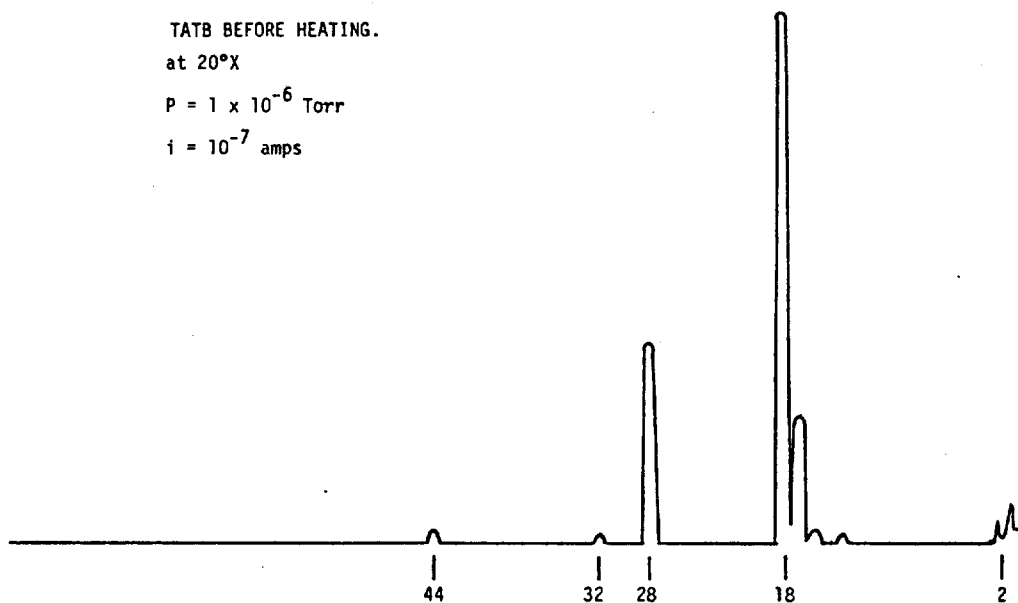


Figure 5. Residual gas spectra from pure TATB.

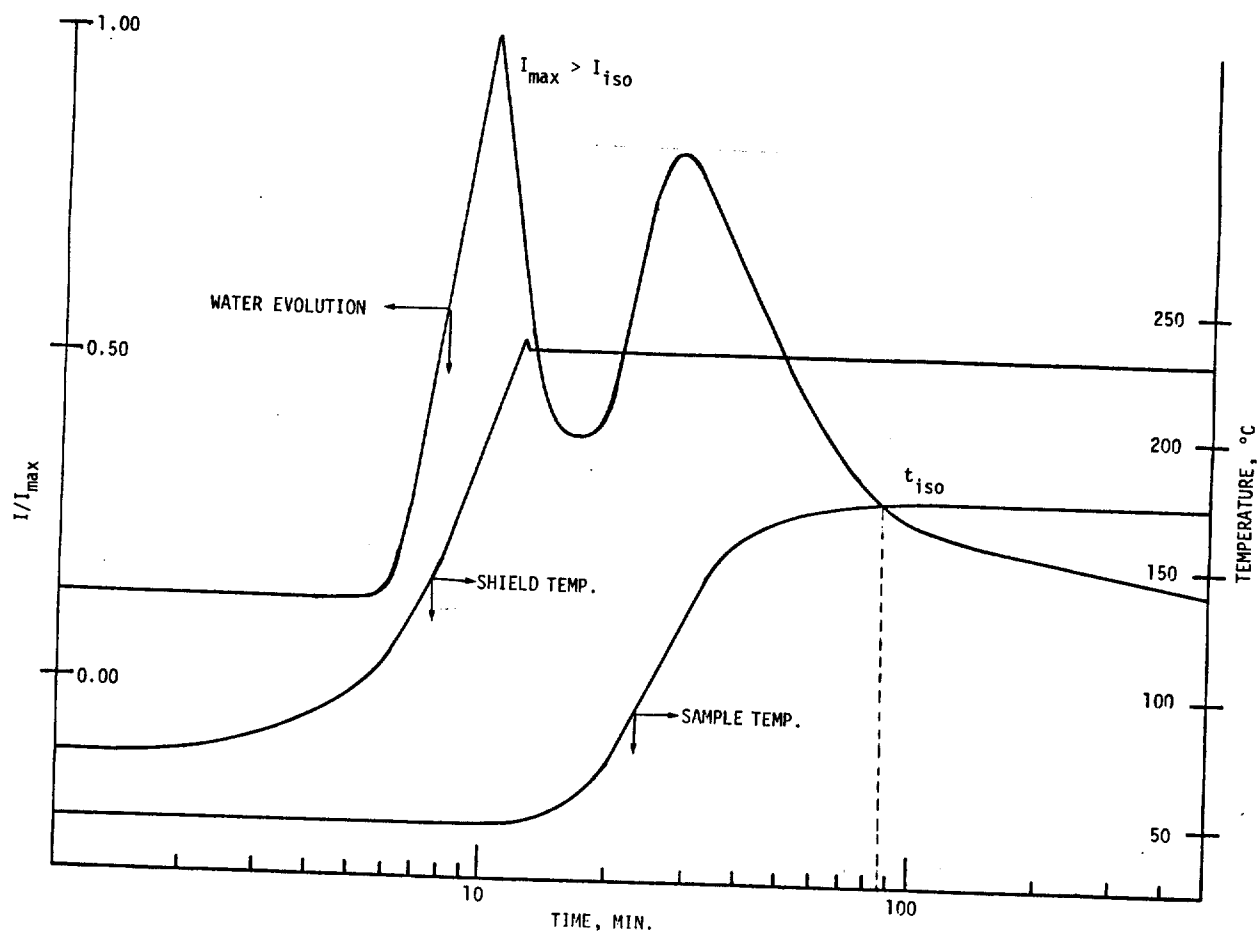


Figure 6. Evolution of water from TATB at 175°C.

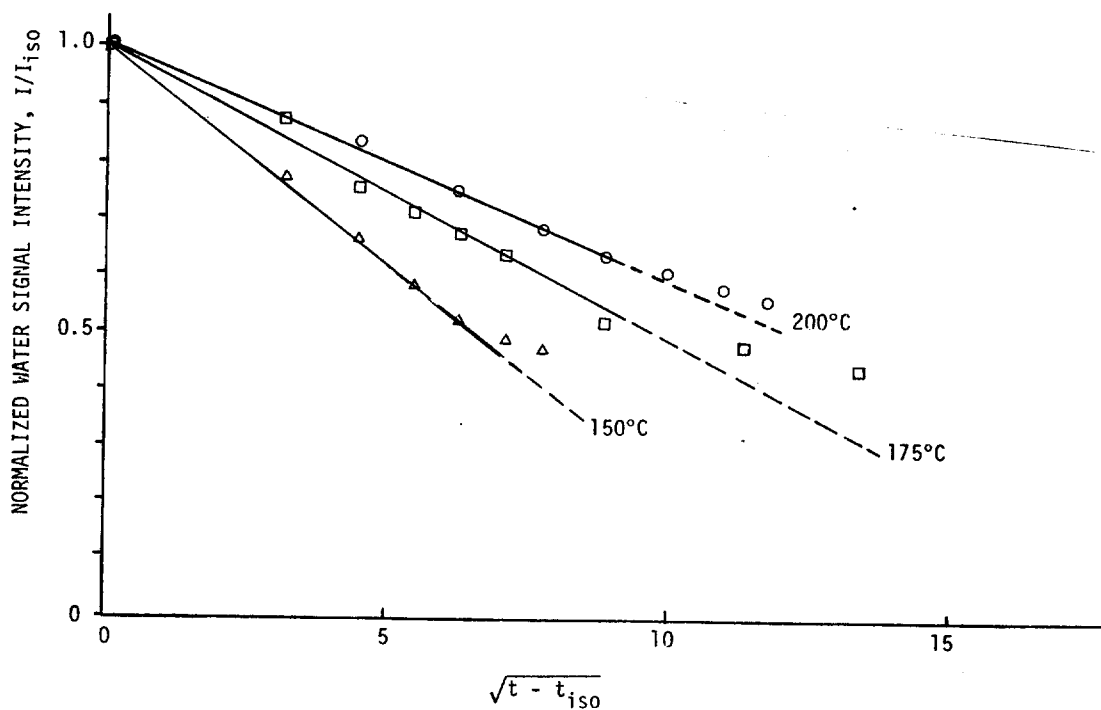


Figure 7. Evolution of Water from TATB

Thus,

$$I/I_{iso} \propto -\sqrt{t - t_{iso}} \quad (3)$$

where,

- t = time
- t_{iso} = time at beginning of isothermal conditions
- I = intensity of mass 18 in RGA output
- I_{iso} = intensity of mass 18 in RGA output at t_{iso}

It can be seen that the early time data are reasonably well described by a diffusion process.

Depletion of water at later times is shown by the deviation of the experimental points from a straight line. The intensity of mass 18 at long times approaches the water background of the vacuum system.

DISCUSSION

The vapor pressure and heat of sublimation for TATB obtained in our study compare well with the results of Rosen & Dickinson, who used the Langmuir technique in their studies. There is a fundamental difference between the Langmuir and Knudsen effusion methods, because a true solid-gas equilibrium is established in the latter effusion method but not in the former method; nevertheless, the results are comparable.

The vapor pressures of the three explosives are virtually identical at 200°C. At 175 and 150°C the pressure of the two PBX's exhibit a divergence from the pure TATB line. This is most notable for the RX03-DI and is probably due to low temperature outgassing of the polymer binders. Outgassing of the phenoxy binder alone at 150°C showed an effusion rate of volatiles, mostly water, that was about equal to that of the RX03-DI PBX, namely, 7×10^{-9} g/cm² sec.

Examination of the residual gas spectra in Figure 5 at 20, 150, and 200°C indicates no essential differences in the composition of gases evolved at these different temperatures. The Mass 40 peak in the spectra at 200°C is due to a small Ar leak into the vacuum system. The early detection of water during heat up is due to system outgassing as shown in Figure 6 by the temperature curves for the shield and sample thermocouples.

The curves in Figure 7 suggests a diffusion controlled process for release of water from TATB. The flattening out of the tails for the same curves show that the water source becomes depleted at long times. The sample water intensity eventually decreases to the same

level as that of the vacuum system background. This implies that there is no water generating process occurring in the explosives tested, within the limit of detectability of the RGA.

CONCLUSION AND FUTURE WORK

We can draw three general conclusions from our study. First, the vapor pressure and heat of sublimation for TATB are in fair agreement with literature values, even though the techniques are different. Second, in vacuum the evolution of volatile species of TATB by itself at elevated temperatures (150-200°C) or by interaction with either the Kel-F or Phenoxy binders is small compared to the sublimation of TATB. Third, the evolution of water from TATB appears to be controlled by diffusion and is from a limited source. Typical values are 0.04 wt% H₂O in pure TATB and 0.002 wt% H₂O in a Kel F PBX.^{2,3}

For future work we plan to conduct TGA measurements on Kel-F800 and phenoxy PKHJ binders alone and search for TATB-binder interactions by Knudsen effusion of pure and mixed components. The reproducibility of our measurements on TATB, RX03-BB and RX03-DI will be examined also.

REFERENCES

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2. H. Leider, "Summary of Activities for Compatibility Project, May, 1976," LLL General Chemistry Division Document COCC:76-11, May 28, 1976.
3. C. Colmenares and L. C. McDavid, Equilibrium Water Vapor Pressure and Total Moisture Content Measurements on TATB, LLL Report UCID 17049, February 23, 1976.

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